966. *Peroxy-complexes of Inorganic Ions in Hydrogen Peroxide–Water Mixtures. Part IV.*[1] *Decomposition by Tungstate Ions.*

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pH, spectrophotometric, and gas-evolution studies have shown that, over a wide range of hydrogen peroxide–water mixtures, the tungstate ion is present as a single peroxy-complex. This exists in two conjugate forms, probably WO_8^{2-} and HWO_8^-. The dissociation constant of the HWO_8^- ion has been measured over a range of solvent compositions. The weak catalytic power of the tungstate ion has been found to be due to a reaction between the WO_8^{2-} ion and a water molecule.

The behaviour of chromate and molybdate ions in hydrogen peroxide–water mixtures has been studied recently.[1,2] Despite its weak catalytic power the corresponding action of the tungstate ion is of interest in order that the detailed decomposition kinetics of peroxy-ions of the metals within a single group of the Periodic Table may be compared.

Jahr and Lother reported two pertungstates.[3] One, derived from the acid H_2WO_6, is formed in very dilute hydrogen peroxide and is colourless; the other, derived from the acid H_2WO_8, is formed in more concentrated peroxide and is yellow. Under the conditions of the present investigation only one peroxy-complex is observed. Since the doubly ionized form of this complex is yellow, it is assumed to be the dissociated form of Jahr and Lother's second complex WO_8^{2-}. The conjugate acid, HWO_8^-, is colourless.

Extensive kinetic studies at low hydrogen peroxide concentrations have been reported by Bogdanov.[4] Two peroxy-complexes were postulated, and the observed maximum decomposition rate at about 10% hydrogen peroxide was attributed to maximum formation of the lower, but more active, complex. Little comparison can be made with the concentrated hydrogen peroxide–water mixtures of the present investigation.

Experimental

B.D.H. "AnalaR" sodium tungstate was used without purification. Recrystallisation from water did not appreciably alter its catalytic activity. The other materials have been described elsewhere.[2]

The techniques were similar to those of the investigation of the molybdate ion.[1] The weak catalytic power of the tungstate ion made necessary the use of comparatively high concentrations, usually 0·1M. Concentrations of perchloric acid (if any) were also of this order of magnitude, and the ionic strength was kept constant at 0·5 with sodium perchlorate.

Measurement of pH and optical absorption presented no greater problem than in the earlier investigations. The decomposition rates were of the same order of magnitude as in the molybdate investigation, and the gas-evolution measurements required corresponding care. The decomposition rate was measured first with all constituents present except the sodium tungstate solution, and then 24 hr. after addition of this catalyst. The difference was taken as the rate which is due only to the tungstate catalysis. In experiments with sodium hydroxide present in concentrations up to 5×10^{-2}M the initial rate due to the base-catalysed decomposition was large compared with the increase in rate on addition of tungstate ions, and the figures obtained by difference were too scattered for interpretation. However, pH and spectrophotometric measurements showed the tungstate species to be the same as in neutral solution, and it is inferred that in alkaline solution tungstate is present as the doubly charged peroxy-ion, WO_8^{2-}. Only in acid solution have the results been given quantitative interpretation.

As in the earlier papers, concentrations are expressed in mole fractions. Molarity has been retained only in qualitative descriptive passages, and in Fig. 1, where the catalyst concentration of each of the three solutions depicted is 0·1M, but where these concentrations would no longer be identical if the units were converted into mole fractions.

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[1] Part III, Dedman, Lewis, and Richards, *J.*, 1963, 2456.
[2] Flood, Lewis, and Richards, *J.*, 1963, 2434.
[3] Jahr and Lother, *Ber.*, 1938, **71**, 894, 903, 1127.
[4] Bogdanov, *Zhur. obshchei Khim.*, 1947, **17**, 887; *Zhur. fiz. Khim.*, 1950, **24**, 1450; 1951, **25**, 49.

RESULTS AND DISCUSSION

pH *Measurements.*—Addition of sodium tungstate to neutral hydrogen peroxide produces only a small increase in the pH of the system; this indicates that most of the peroxy-ions which are formed are doubly charged anions. Addition of sodium hydroxide to a neutral solution containing sodium tungstate produces pH changes which do not noticeably differ from those produced by sodium hydroxide when no tungstate is present. The doubly charged anion appears to be the stable entity in both neutral and alkaline solutions. However, addition of perchloric acid to the system produces pH changes which are less than those which would be observed in the absence of sodium tungstate. This is due to the formation of the singly charged anion, HWO_8^-.

The acid dissociation constant of this ion,

$$K = [H^+][WO_8^{2-}]/[HWO_8^-]$$

has been calculated over a range of hydrogen peroxide–water mixtures by the application of the formula

$$K = [H^+]([W] - [H_s^+] + [H^+])/([H_s^+] - [H^+]), \qquad (1)$$

where $[H^+]$ is the measured hydrogen-ion concentration, $[H_s^+]$ is the stoicheiometric concentration of added perchloric acid, and [W] is the total tungstate concentration. The values of K so calculated at chosen hydrogen peroxide concentrations were found to be independent of the value of $[H_s^+]$, which showed that within the range investigated ($[H_s^+]$ = 0·2—0·1M) the second hydrolysis to H_2WO_8 was negligible.

The values for K at several hydrogen peroxide concentrations are listed in the Table. Also given at each concentration are the values of the hydrolysis constant of the WO_8^{2-} ion, defined by

$$K' = [HWO_8^-][O_2H^-]/[WO_8^{2-}]$$

and related to K by the expression $K' = K_m/K$, where K_m is the autoprotolysis constant of the solvent.

		pH detn.		Spectrophotometric detn.	
H_2O_2	$10^{13}K_m$	10^6K	$10^8K'$	10^6K	$10^8K'$
0·810	0·48	6·12	0·79	6·1	0·79
0·609	3·1	11·4	2·7	9·7	3·1
0·447	3·9	14·0	2·8	10·0	3·0
0·345	3·8	4·9	7·8	3·7	10·3
0·252	2·5	3·2	7·8	2·8	8·9
0·120	0·49	0·56	8·5	0·51	9·7
0·056	0·18	0·14	12·9		

Spectrophotometric Measurements.—The yellow colour obtained on dissolving sodium tungstate in neutral or alkaline hydrogen peroxide gradually disappears as perchloric acid is added. Thus the colour is due to the basic (anionic) species of an acid–base equilibrium. Spectrophotometric studies of the yellow solutions revealed no peak in the optical absorption in the visible region of the spectrum (the only region available for study owing to the high absorption of hydrogen peroxide itself in the ultraviolet region). However, absorption begins to increase markedly at wavelengths below about 450 mμ, owing presumably to a peak in the ultraviolet region. No significant absorption could be measured at the visible wavelengths for the highly acid, colourless, tungstate solutions. All subsequent work was carried out at 410 mμ. All absorption at this wavelength may be taken as due to the WO_8^{2-} ion. Since the absorption reaches a constant value in slightly alkaline solutions, which may be interpreted as due to quantitative formation of the WO_8^{2-} ion, the lower absorption in a slightly acid solution gives a direct measure of the WO_8^{2-} concentration in the equilibrium mixture. The concentration of the non-absorbing HWO_8^- ion may then be found by difference. Beer's law was obeyed throughout the range studied, indicating that the pertungstate ions show no tendency towards polymerization, although some workers have postulated the formation of a dimer in very weak hydrogen peroxide.[5,6]

Values of K were calculated in which the concentrations of WO_8^{2-} and HWO_8^- were obtained in this manner and the value of $[H^+]$ obtained from parallel pH measurements. These are also listed in the Table.

Rate of Decomposition.—The decomposition rate responded to treatment similar to that applied in the molybdate investigation.[1] At constant hydrogen peroxide concentration the decomposition rate, when plotted against the optical density (itself a measure of the WO_8^{2-} ion concentration), gives a straight line passing close to the origin, showing that the doubly charged WO_8^{2-} ion is responsible for catalysis. However, as in the case of the molybdate-ion catalysis, the proportionality constant between rate and optical density varies, becoming smaller as the hydrogen peroxide concentration is increased.

Fig. 1 shows typical plots of rate against optical density at three hydrogen peroxide concentrations, and Fig. 2 shows the variation in the slope of such lines against the water component of the solvent mixture. This curve is similar in shape to the corresponding curve obtained for molybdate ion. Although there is a large increase in the proportionality constants obtained from Fig. 1 with increasing water concentration, only a very rough approximation to a first-order relation may be inferred. Slightly better linearity is obtained by plotting the slopes of Fig. 1 against the activity rather than the concentration of the water component. But since only one peroxy-complex is present, and the concentration of the active ionized form of this has been taken into consideration in obtaining the slopes of Fig. 1, it is necessary to introduce the water concentration into the final rate equation in a manner similar to that postulated in the molybdate and chromate investigations.

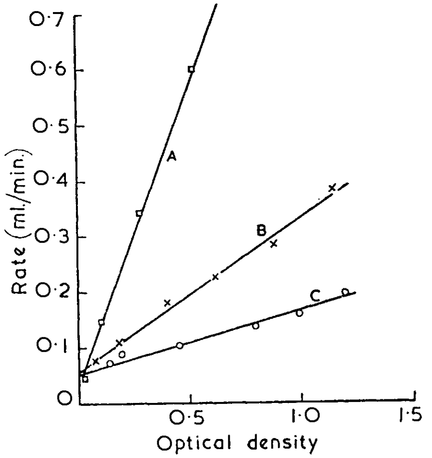

FIG. 1. Rate of decomposition, plotted against optical density for H_2O_2 concentrations, (A) 0·120M, (B) 0·447M, and (C) 0·810M.

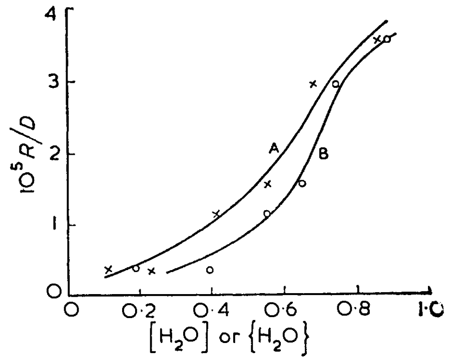

FIG. 2. Rate/colour, plotted against (A) activity and (B) concentration of water in admixture with hydrogen peroxide.

Thus the rate equation may be written

$$WO_8^{2-} + H_2O \xrightarrow{k} \text{Products}$$

and the kinetic equation becomes

$$-d[H_2O_2]/dt = k[WO_8^{2-}][H_2O]$$

If all concentrations are expressed as mole fractions and t is in minutes, then $k = \sim 0{\cdot}02$,

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[5] Souchay, *Bull. Soc. chim. France*, 1949, 122.

[6] Jahr and Blanke, *Z. anorg. Chem.*, 1953, **272**, 45.

to be compared with 0·3 in the analogous molybdate investigation and 7 in the reaction between the $HCrO_5^-$ ion and water.

Considered in isolation, the kinetic data could be explained very adequately by Bogdanov's theory of two peroxy-acids. Our reasons for preferring the interpretation in which the anionic form of a single peroxy-acid reacts with a water molecule are as follows.

On Bogdanov's theory the reduction in rate with increase in hydrogen peroxide concentration is due to the increasing formation of a higher, but less active, peroxy-acid. However, examination of both pH and spectroscopic data shows that over the same range of solvent composition there is no marked continuous variation in the apparent acid dissociation constant of the catalyst per-acid, and the variations which are observed are shown by both methods. If two peroxy-complexes are indeed present, as Bogdanov suggests, then they must have very similar acid dissociation constants and optical absorption spectra. Further, in the more complicated mechanism of chromate catalysis an analogous mechanism has been shown to take place. In this case, to fit the data to a Bogdanov-type mechanism, it would be necessary to postulate that, in addition to the peroxy-acids' having the same dissociation constants and absorption spectra, the rate constants for their reaction with the hydroperoxyl ion (O_2H^-) should be the same for each. The existence of two peroxy-acids, resembling each other in all studied properties except rate constant for first-order decomposition, appears to us to be unlikely.

General.—The ionization of the peroxy-acids of the Group VI metals in hydrogen peroxide–water mixtures has been shown to increase in the order: $Cr < Mo < W$. This is the reverse of the behaviour of the non-peroxidated oxygen acids of these metals in water:[7] $Cr > Mo > W > U$. This is the general pattern for the oxygen acids of metals in the same group in the Periodic Table, although quantitative comparisons cannot be made for the oxygen acids of Group VI owing to their great tendency to form polymeric species in aqueous solution. In this respect they differ from the peroxy-acids in hydrogen peroxide–water mixtures, where no evidence of polymerization has been observed in the three cases studied. The inversion of the relative ionization of the peroxy-acids from that of the simple oxygen acids may be explained on the basis that the inductive effect of the central metal atom is not greatly effective through the O–O bond, and the increasing stability of the anion of the peroxy-acids of the heavier metals is simply due to their larger size and increased distribution of charge.

The ionization constant of an oxygen acid in water and of the corresponding peroxy-acid in hydrogen peroxide–water mixtures may only be compared in the case of the chromate and perchromate ions, since no figures are available for the ionization of molybdic and tungstic acid in water. The several published values for the dissociation constant of chromic acid in water,[8] although differing by more than an order of magnitude, are all larger than the figure obtained for the ionization of perchromic acid in hydrogen peroxide. That the peroxy-acids are weaker than the corresponding oxygen acids has been indicated by the measurement of the dissociation constants of organic per-acids in water.[9]

In the present investigation the general trend in the variation of K with hydrogen peroxide concentration is the same as that observed in the analogous work on molybdate. A maximum is reached at intermediate peroxide concentrations, with significant reductions at either end of the concentration range. Both differ from the variation of the apparent ionization constant of chromic acid in hydrogen peroxide–water mixtures, where the steady fall with decreasing hydrogen peroxide concentration has been interpreted as due to the equilibrium between two complexes that have different degrees of peroxidation. Emphasis must be placed on the fact that the dissociation constant in the case of chromate refers to that of a non-ionized species going to a hydrogen ion and a single-charged anion, whereas

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[7] Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, Vol. II, 1950, p. 999.

[8] "Stability Constants. Part II. Inorganic Ligands," *Chem. Soc. Special Publ.*, No. 7, 1958, p. 29.

[9] Everett and Minkoff, *Trans. Faraday Soc.*, 1953, **49**, 410.

in the case of both molybdate and tungstate an ion already having a single negative charge dissociates into a hydrogen ion and a doubly charged anion. The evidence from all three investigations is that peroxidation is virtually complete in all ionized forms of the complex, and that only in non-ionized forms can significant amounts of non-peroxidated species be present in hydrogen peroxide–water solution.

The values of K' in the present investigation are less constant than they are for molybdate. This may be because the critical equilibrium takes place in acid solution, where the role of the O_2H^- ion, which appears in the hydrolysis but not in the dissociation equation, is likely to be small. The critical molybdate equilibrium takes place in alkaline solution, and here the direct effect of the O_2H^- ion would be expected to be greater.

We turn now to the stability of the peroxy-acids and their effectiveness as catalysts in the decomposition of hydrogen peroxide. The relationship noted by Melikov and Jeltschaninov,[10] that the stability of peroxy-acids within a group of the Periodic Table increases with increasing atomic weight, is clearly corroborated. As a catalyst, the perchromate ion is an order of magnitude stronger than the permolybdate ion, which is itself an order of magnitude stronger than the pertungstate ion. In most other respects the kinetics of decomposition are similar in the three cases. Each may be interpreted as a reaction between the more anionic of the species present and a water molecule, and hence decomposition rate increases with decreasing acidity and decreasing hydrogen peroxide concentration. In the case of the perchromate ion only, the picture is complicated by direct reactions between the peroxy-anion and a perhydroxyl ion and the first-order decomposition of the undissociated peroxy-acid. No reliable decomposition results could be obtained in alkaline tungstate solution, but in the case of the molybdate reaction there is definitely no reaction between a MoO_8^{2-} ion and a hydroperoxyl ion comparable with the perchromate case.

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[10] Melikov and Jeltschaninov, *Ber.*, 1909, **42**, 2291.